N-Ethylmorpholinium Molybdates & Tungstates

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N - Ethylmorpholinium - tetramolybdate, tetratungstate, tetrathiomolybdate and tetrathiotungstate have been prepared and characterized on the basis of elemental analyses, X-ray powder patterns and UV, visible and IR spectral measurements. The thermogravimetric analysis suggests that, in air, the compounds give the metal trioxides as the final products of decomposition. In nitrogen atmosphere the thiosalts give the metal disulphides.

MOLYBDENUM and tungsten form several isopolyoxyanion[1] and chalcogenometallates[2,3] containing alkali metal and ammonium cations. As a part of investigation on the stabilization of complex anions with bulky cations, we have reported[4] the characterization of morpholinium molybdates and tungstates recently. The results of studies on the stabilization of tetramolybdate, tetratungstate, tetrathiomolybdate and tetrathiotungstate ions by N-ethylmorpholinium, [emfH$^+$], counter cation are presented in this paper.

N-Ethylmorpholine, molybdic oxide and tungstic oxide were E. Merck samples. All the other chemicals used were of AR grade. N-Ethylmorpholinium tetramolybdate and tetratungstate were prepared by reacting the respective metal trioxides with 50% aqueous N-ethylmorpholine in 1 : 5 ratio. The contents were warmed if necessary to dissolve the oxides and the solution filtered to remove the suspended particles. The filtrates were kept *in vacuo* for 2-3 days and the separated crystalline products were filtered, washed successively with acetone and ether and air-dried.

N-Ethylmorpholinium-tetrathiomolybdate and tetrathiotungstate were prepared by passing hydrogen sulphide for 4-6 hr through the respective N-ethylmorpholinium metallate solutions containing a small amount of free base. The separated red crystals of tetrathiomolybdate and golden yellow crystals of tetrathiotungstate were collected on a filter, washed with a mixture of acetone and ether and air-dried. The analytical data of the compounds are given in Table 1.

The X-ray diffraction patterns of the compounds were recorded on a Philips PW 1041 X-ray diffractometer using Cu-K_α radiation. The electronic spectra of the thiosalts were recorded in water on a Beckman DK 2 spectrophotometer. The infrared spectra (pellet) of the compounds were measured on a Perkin Elmer 225 spectrophotometer. The far IR (nujol) spectra of the thiosalts were taken on a Beckman IR 11 spectrophotometer in the range 35-200 cm^{-1}. The thermogravimetric analyses were carried out in air and nitrogen atmosphere on a Netzsch thermal analyser.

Tetramolybdates and tetratungstates are readily soluble in water, and on acidification the respective metal trioxides are precipitated. The usefulness of Mo-O stretching frequencies in the elucidation of coordination around molybdenum in the molybdates has been illustrated by Gatehouse and Leverette[5] and Caillet and Saumagne[6]. Several multiple bands observed in the region 950-650 cm^{-1} for $[emfH]_2Mo_4O_{13}$ are characteristic of six-coordinated molybdenum as noticed[5] in the case of $K_2Mo_4O_{13}$. The IR spectral frequencies due to metal-oxygen stretching in $[emfH]_2Mo_4O_{13}$ appear at: 948s, 916 h, 909s, 860sh, 840m, 732 h, 710s, 662m, 598w, 572 h, 525w, 460w, 372m, 358m and in $[emfH]_2W_4O_{13}$ these appear at 950sh, 930s, 875s, 770s and b, 615w, 598w, 375m and 325m cm^{-1}. These bands were assigned to $\nu M-O$ by comparing the spectra of the complexes with that of free N-ethylmorpholine.

The X-ray powder patterns of tetratungstate show very few and weak lines suggesting poor crystallinity of the compound. The *d* spacings indicate that ethylmorpholinium tetramolybdate and tetratungstate are not isostructural. The absence of isomorphism is also observed in the corresponding potassium analogues; $K_2Mo_4O_{13}$ consists[5] of infinite chains of edge sharing distorted MoO_6 octahedra whereas $K_2W_4O_{13}$ is made up[7] of six-membered rings of corner sharing WO_6 octahedra. The similarity of Mo-O spectral bands observed in $K_2Mo_4O_{13}$ and $[emfH]_2Mo_4O_{13}$ indicates that the Mo-O net work in the two compounds are similar.

The thermal studies on tetramolybdate and tetratungstate in air showed that these compounds start decomposing around 180° and the decomposition is complete at 400°. The final decomposition products were examined by X-ray and chemical methods and were found to be metal trioxides. The observed weight losses are 70 and 79% for the molybdate and tungstate respectively and those expected for the formation of $M^{VI}O$ are 69·9 and 78·6% respectively.

The tetrathiosalts are highly soluble in water and on acidification yield the precipitates of respective metal trisulphides. The salts give out hydrogen sulphide and the base on keeping, resulting in the formation of metal trisulphides. The *d*-spacings of the thiosalts suggest that these are isostructural, similar to those of alkali metal and ammonium tetrathiomolybdates and tetrathiotungstates[8,9].

TABLE 1 — ANALYTICAL DATA OF N-ETHYLMORPHOLINIUM METALLATES

Compound	Found (calc.)				
	C (%)	H (%)	N (%)	N (%)	Mo/W (%)
$[emfH]_2Mo_4O_{13}$	17·3 (17·5)	3·48 (3·42)	3·59 (3·40)	—	46·0 (46·8)
$[emfH]_2W_4O_{13}$	12·2 (12·3)	2·73 (2·40)	2·41 (2·39)	—	62·7 (62·6)
$[emfH]_2MoS_4$	31·1 (31·6)	6·83 (6·33)	6·07 (6·14)	28·4 (28·1)	21·5 (21·0)
$[emfH]_2WS_4$	26·3 (26·5)	5·42 (5·18)	5·37 (5·15)	24·0 (23·6)	34·0 (34·8)

The electronic spectra of thio compounds show three characteristic bands with the molar absorptivities of the order of 10^4 at 465, 317 and 214 nm in the case of tetrathiomolybdate and at 389, 274 and 214 nm in the case of tetrathiotungstate. These high-intensity bands are due to charge-transfer and are assigned to the transitions $t_1 \rightarrow 2e(\nu_1)$, $t_1 \rightarrow 4t_2(\nu_2)$ and $3t_2 \rightarrow 2e(\nu_3)$ respectively according to the Viste-Gray MO scheme[10]. The νM-S frequencies in the IR are reported to appear[11] in the range 450-500 and around 180 cm^{-1} for the thiomolybdates and thiotungstates. The strong intensity IR absorptions observed at 476, 462 and 195 cm^{-1} for thiomolybdate and 488, 466 and 187 cm^{-1} for thiotungstate salts are assigned to M-S stretching frequencies in the present compounds.

The thermal studies of the thiosalts were carried out, both, in air and nitrogen atmosphere. The two compounds exhibited similar decomposition behaviour for a particular atmosphere and the thermal behaviour was similar to that of ammonium[12] and morpholinium[4] tetrathiometallates. The salts decompose in two distinct steps, the first involving the formation of trisulphides and the second step involving its subsequent decomposition. Both in air and nitrogen, the salts start decomposing around 180° giving hydrogen sulphide as one of the gaseous products. The first stage of decomposition is complete by 350°. The weight losses noticed at this stage in both the atmospheres are 57 and 48% respectively for the thiomolybdate and thiotungstate. The expected weight losses for the formation of trisulphides are 57·9 and 48·5% respectively. On further increase in temperature, the trisulphides start decomposing in air to give the metal trioxides around 500°. The weight loss curves indicated 68 and 57% loss for the thiomolybdate and the thiotungstate and the expected weight losses for the formation of $M^{VI}O_3$ are 68·5 and 57·4% respectively. In nitrogen atmosphere, the weight loss recorded around 500° for N-ethylmorpholinium thiomolybdate was 65% and that for the corresponding thiotungstate was 54%. The calculated weight losses for the formation of corresponding metal disulphides are 64·9 and 54·6% respectively. The chemical and X-ray analyses confirmed the formation of $M^{VI}O_3$ in air and $M^{IV}S_2$ in nitrogen atmospheres.

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Physico-chemical Properties of Vegetable Proteins: Part IV— Flocculation of Protein Sols Stabilized at Different *p*H Values by Electrolytes

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Flocculation of a few vegetable protein sols stabilized at *p*H 11 and 7·5 by different electrolytes has been studied. The higher flocculation values are obtained for cations like Ca^{2+}, Sr^{2+} and Ba^{2+}, while lower values are obtained for cations like Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Ag^{+}. Protein fractions obtained with aq. NaCl yield more stable sols than the whole proteins etxracted from the same source with aq. NaOH. The flocculation values of various electrolytes for the sols stabilized at *p*H 2·5 show that amongst anions of a given valency, the one with a larger size is a more effective flocculent.

SEVERAL investigations relating to flocculation of sols of animal proteins such as haemoglobin[1], egg albumin[2], gelatin[2,3] and casein[4,5] by electrolytes have been reported in the literature. Similar work on vegetable proteins, however, has not received adequate attention. This prompted us to undertake the present work.

Two varieties of soybean proteins and their respective glycinin fractions; peanut protein and its major fractions (arachin and conarachin), and gliadin and glutenin fractions of wheat protein (gluten, BDH) were used. The methods employed for the isolation of these proteins were the same as described earlier[6].

Sols of 0·5% concentration at *p*H 11 and 7·5 were prepared by suspending the required amounts of proteins in 20 ml of CO_2-free dist. water, and adding enough of NaOH solution gradually with continuous stirring to dissolve the protein and raise the *p*H to about 11·5 in one set of experiments and to *p*H 8 in the second set. The excess of the alkali was removed by dialysis till the *p*H was brought down to 11·0 in the first case and 7·5 in the second case. Sols were also prepared at *p*H 2·5 following the same procedure except for using dil. HCl in place of NaOH.

Two ml aliquots of a given sol were added to several 3 ml portions of the solutions of increasing concentrations of a given electrolyte, and after shaking allowed to equilibrate at $30° \pm 0·01°$ for 10 min. The minimum concentration of the electrolyte at which the turbidity appeared was noted. The process was repeated several times.

The flocculation values of different electrolytes, expressed as moles/10^5 g protein, for the sols of 0·5% concentration are presented in Table 1. The flocculation values for the sols at *p*H 7·5 are much lower as compared to the values at *p*H 11·0 because of a much smaller number of acid groups ionizing at this stage[7]. Since the protein sols carry negative charge